

Abstract

Kinetics of the first order phase transition has been investigated. The case when the droplets sizes have a limit value is considered. An analytical theory for such process has been constructed and all main characteristics of the process have been determined by rather simple approximate analytical formulas. The limit for a droplets size violates the avalanche consumption of the mother phase which is the basic feature of the first order phase transition and have been actively used in previous publications. Now one can not state that the main quantity of the already condensed substance is contained in the droplets formed under conditions unperturbed by nucleation process. This requires to introduce some new methods of solutions for kinetic equation which are given in the present paper.

Kinetics of nucleation under the break of the blow-up growth

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1 Introduction

The most interesting feature of the first order phase transition is the global kinetics of transformation of a mother phase into a state of objects of a new phase. Traditionally the theoretical description of the first order phase transition kinetics is given on example of nucleation [6]. Then the mother phase is a supersaturated vapor and the new phase is a liquid phase. The driving force of the first order phase transition is initiated by metastability which is traditionally described by the value of a supersaturation ζ . The last is the ratio of the density of surplus vapor and the density of the saturated vapor minus one unit.

Kinetics of nucleation has been already investigated in the case of the ordinary (unlimited) phase transition. In that case the property of the blow-up growth has been actively used [1]. This property means that the rate of growth of the molecules number inside the droplet for a given droplet rapidly increases in time. It grows so rapidly, that even acceleration of the rate of growth also grows in time. This property leads to two important consequences, which allow to give an analytical description of the nucleation period. These consequences are the following:

- The nucleation period (i.e. the period of rather intensive appearance of supercritical droplets) is well localized in time.
- The droplets appeared in the first moments of nucleation period contain the main quantity of molecules (in comparison with other droplets) during the nucleation period. These first moments can be called as the pre-nucleation period. During the pre-nucleation period the droplets don't essentially perturb the state of the system. This allows to calculate the characteristics of droplets appeared during the pre-nucleation period.

For example, the regime of the unlimited free molecular growth has the mentioned feature. Namely here the number of molecules ν inside the supercritical embryo (i.e. inside the droplet) grows in time t as

$$d(\nu)^{1/\alpha}/dt = \zeta/\tau, \quad \alpha = 3, \quad (1)$$

where τ is a characteristic constant which has a sense of a mean time between collisions of a given molecule in saturated vapor with other molecules. This type of growth is wide spread in nature. Later we shall use this type of growth as a model for concrete formulas.

In previous theories for nucleation kinetics (see review in [1]) it was supposed that the sizes of droplets can become in principle infinitely big. Here we consider the opposite situation. In many systems the process of the droplets growth is limited by some artificial restrictions. The number ν of molecules inside the droplet can not be greater than some value ν_{lim} , which is an external parameter of the theory. We imply that ν_{lim} strongly exceeds the number ν_c in the critical embryo under the supersaturation which corresponds to relatively intensive appearance of droplets (this condition will be specified). The existence of a limit size takes place in the processes of cementation, of condensation in an external lattice, morphological transitions, etc. This type of transition is rather wide spread in nature. Kinetics of this process will be investigated in this paper.

The limit of droplets sizes leads to the loss of the blow up property of growth in the global kinetics of nucleation. From the first point of view it seems that the introduction of a limit size can not essentially change the approaches of description, but it is an illusion and below some principally new methods of solution of kinetic equations have to be presented.

This publication continues the set of articles devoted to the construction of the global kinetics of a phase transition (see [1]). To grasp the current approach it would be useful to come through these papers. We use all physical assumptions from these papers except explicitly mentioned ones. All definitions of physical characteristics can be taken also from [1].

Traditionally two characteristic types of external conditions are considered. The first type is a decay of a metastable state [2]. Here at the initial moment of time we have the metastable phase with no objects of a new phase in the system. Later there will be no external influence on the system. The process of nucleation begins and the appearance and growth of droplets cause the fall of supersaturation which stops the further intensive nucleation.

The second type is nucleation under the smooth variation of external conditions. At first moments of time the increase of supersaturation by the action of external conditions is greater than the decrease due to the mother phase consumption by the droplets. But the vapor consumption has a very rapidly increasing intensity and later the mentioned decrease will overtake the mentioned increase and the supersaturation will go down. The process of intensive nucleation will stop. We are going to describe kinetics of the process in both situations.

We shall use the following law of droplets growth for $\rho \equiv \nu^{1/3}$:

$$\begin{aligned} \frac{d\rho}{dt} &= \zeta/\tau \quad \text{for } \rho < \rho_{lim} \equiv \nu_{lim}^{1/3} \\ \frac{d\rho}{dt} &= 0 \quad \text{for } \rho \geq \rho_{lim} \equiv \nu_{lim}^{1/3} \end{aligned}$$

Rigorously speaking it would necessary to determine the variable which has the velocity of growth independent on the value of this variable. We shall act in another manner: at first we suppose that there is no limitation on growth and then calculate the number of molecules in a droplet by a "curved" formula.

Here it is possible to introduce the following variables: The variable y is the number of molecules in the droplet which is growing without any limit by an initial law (1). The variable z is the value of y for droplet which was born at "initial" moment of time. Certainly, for every droplet $\nu < z$. The variable x is defined as $y = z - x$. Then we see the correspondence between t and z and the correspondence between t and x . The values z and x are now equivalent.

The number of molecules ν inside the droplet has to be calculated now as

$$\nu = (z - x)^3 \quad \text{for } z - x < \rho_{lim}$$

and

$$\nu = \nu_{lim} \quad \text{for } z - x > \rho_{lim}$$

We see that here there is no unique analytic dependence and this will seriously complicate the evolution equation.

We have also to mention that the property of the effective size of growth which was observed in recent publication [3] in construction of kinetics for the law (1) with small $\alpha \leq 1$ also doesn't take place. For droplets with¹ $\nu \gg \nu_{lim}$ such a property is observed, but for droplets with $\nu < \nu_{lim}$ is the opposite property of the blow-up regime takes place. Namely the situation where both regions are important in substance balance is interesting.

All analytical constructions are based on the following approximation for the rate of nucleation I as a function of supersaturation:

$$I(\zeta) = I(\zeta_0) \exp(-p(\zeta - \zeta_0)) \quad (2)$$

Here ζ_0 is the base of decomposition and the positive parameter p is defined as

$$p = -\frac{dF_c}{d\zeta}|_{\zeta=\zeta_0}$$

where F_c is the free energy of a critical embryo. The last approximation is not more than the Klapeiron-Klausius approximation, but it is written for special variables. The validity of this approximation has been discussed in [1].

2 Decay of metastable state

Now we shall consider the situation of decay. The initial value of supersaturation will be marked by Φ . The base of decomposition ζ_0 for function ζ can be chosen as Φ .

¹Here ν is imaginary value calculated purely according to (1).

We skip the derivation of kinetic equation because it is quite similar to the ordinary case without the limit size and can be seen in [4] or in [5]. The kinetic equation for the evolution can be written in the following form:

$$\begin{aligned} \Phi = \zeta(z) + \Theta(z - z_{lim}) \{ & A \int_{z-z_{lim}}^z (z-x)^3 \exp(p(\zeta(x) - \Phi)) dx + \\ & A \nu_{lim} \int_0^{z-z_{lim}} \exp(p(\zeta(x) - \Phi)) dx \} + \Theta(z_{lim} - z) A \int_0^z (z-x)^3 \exp(p(\zeta(x) - \Phi)) dx \end{aligned} \quad (3)$$

Here A is the amplitude value of spectrum, Θ is the Heavisaid's function, $z_{lim} = \rho_{lim}$. Solution of this equation will give the behavior ζ as a function of x . It allows to calculate the number of droplets (in renormalized units)

$$N(z) = \int_0^z \exp(p(\zeta(x) - \Phi)) dx$$

appeared until the moment $t(z)$ (i.e. until the moment when the imaginary front side of the spectrum attains the value z). The most interesting value is the total number of droplets $N(\infty)$ and the error in this value will be the measure of the accuracy of approximate description.

In contrast to the decay with the unlimited growth we shall have here the several stages of the process of decay and the long continuous tail. The meaning of these parts of the process will be clear later and now we shall start with investigation of the first period and have to put initial conditions. Namely, $t = 0$, $\zeta = \Phi$ and there is no droplets in the system.

Now we shall introduce the value of natural length $\Delta_1 x$ as the characteristic width of spectrum without the limit of growth. For this situation we have the following kinetic equation

$$\Phi = \zeta(z) + A \int_0^z (z-x)^3 \exp(p(\zeta(x) - \Phi)) dx$$

which results in the following characteristic width of the size spectrum

$$f \sim \exp(p(\zeta(x) - \Phi))$$

namely

$$\Delta_1 z = \left(\frac{4}{pA} \right)^{1/4} \quad (4)$$

One can see that $\Delta_1 z$ is a function of Φ since $p = p(\Phi)$, $A = A(\Phi)$. It is possible to see three situations:

- (A) $\Delta_1 z \ll z_{lim}$,
- (B) $\Delta_1 z \gg z_{lim}$,
- (C) $\Delta_1 z \approx z_{lim}$.

2.1 The case $\Delta_1 z \ll z_{lim}$

In this case kinetic equation (3) can be reduced to

$$G(z) = A \int_0^z (z-x)^3 \exp(-pG(x)) dx$$

for the function

$$G = A \int_0^z (z-x)^3 \exp(p(\zeta - \Phi)) dx$$

which has the sense of the number of molecules inside the new phase.

This equation is known from unlimited case and can be solved by iterations:

$$G_0 = 0$$

$$G_{(i+1)}(z) = A \int_0^z (z-x)^3 \exp(-pG_{(i)}(x)) dx$$

Calculation gives $G_{(1)} = Az^4/4$ and already the second iteration gives the practically accurate number of droplets

$$N_{(2)}(\infty) \equiv \int_0^\infty \exp(-pG_1(x)) dx = \left(\frac{4}{pA}\right)^{1/4} B, \quad B \equiv \int_0^\infty \exp(-x^4) dx = 0.9$$

The relative error

$$\epsilon(\infty) = \frac{|N(\infty) - N_{(2)}(\infty)|}{N(\infty)}$$

is less than 0.05 in every case which can be analytically proven.

The high accuracy is also attained also for

$$L_i = \frac{3!}{i!(3-i)!} A \int_0^\infty x^i \exp(-pG) dx$$

calculated on the base of the first iteration i.e for

$$L_i \approx L_{i(2)} = \frac{3!}{i!(3-i)!} A \int_0^\infty x^i \exp(-pG_1) dx$$

These values will be important later.

But this doesn't complete the investigation as in the case of unlimited growth. Earlier or later the droplets sizes attain ν_{lim} and the droplets stop to grow. Then the final value of the supersaturation will be

$$\zeta_{fin\ 1} = N(\infty) \nu_{lim}$$

Here index 1 points that we investigate the first part of the nucleation period.

The time of attaining ζ_{fin} can be easily calculated on the base of monodisperse approximation². The last approximation leads to equation

$$AN(\infty)z^3 = \Phi - \tau \frac{dz}{dt} \tag{5}$$

²The validity of monodisperse approximation can be proved analytically.

which can be easily integrated (as the first order differential equation without explicit dependence on the argument):

$$\int_0^z \frac{dx}{\Phi - AN(\infty)x^3} = t$$

The integral can be taken analytically and gives $z(t)$. Condition

$$z^3(t_{fin}) = \nu_{lim}$$

gives the value of the end t_{fin} of the first part of nucleation. One can compare t_{fin} with the duration of intensive nucleation during the first part, i.e. with

$$\Delta_1 t = \Delta_1 z \tau / \Phi$$

When the inequality $\Delta_1 z \ll z_{fin}$ isn't too strong then the equation (5) isn't suitable because the monodisperse approximation lying in the base of (5) isn't valid even at $z \approx z_{fin}$. Then one has to use instead of (5) the following equation

$$\sum_{i=0}^3 L_i z^3 = \Phi - \tau \frac{dz}{dt}, \quad z|_{t=0} = 0 \quad (6)$$

The methods of solution of this equation are quite similar to the methods of solution of (5) (they are presented in [1]).

While approaching to z_{fin} one has to take into account that L_i begin to change because integration can not be done out of $z < z_{fin}$. These changes can be taken into account by the perturbation technique (because the main influence is given by L_0 which remains unperturbed).

Several important statements can be proved here. They are:

- (A) The process of nucleation takes place in the quasistationary conditions. The time t_1 of essential perturbation of the droplets distribution, which can be estimated as $\Delta z_1 \tau / \Phi$ strongly exceeds the time t_s of establishing the stationary state in the near critical region (more accurate in the region³ $\nu < (2 \div 3)\nu_c$).
- (B) The main role in the vapor consumption is played by the strongly supercritical droplets, i.e. by the droplets with $\nu > (2 \div 3)\nu_c$. These droplets grow regularly with the mentioned law of growth.
- (C) The process of intensive nucleation takes place at $\Phi \geq \zeta \geq \Phi - 1/p$.
- (D) Later the new periods of nucleation (may be not so intensive but long) will take place.

The statements (A), (B) are necessary for construction of the kinetic equation. The statement (C) allows to use the approximation (2). The statement

³To calculate t_s see [6], [7].

(D) requires to continue the consideration of the nucleation process which will be done below.

The last step to do is to give approximation for the number of droplets. After the evident rescaling the kinetic equation can be presented as

$$G = 4 \int_0^z (z - x)^3 \exp(-G(x)) dx$$

The number of droplets appeared until z can be calculated as

$$N(z) = \int_0^z \exp(-x^4) dx$$

We shall use the following approximation

$$N_{appr}(z) = \Theta(0.91 - z)z + \Theta(z - 0.91)0.91$$

The relative error $|N_{appr} - N|/N$ as function of x is drawn in Figure 1. We see that it is small.

2.2 The case $\Delta_1 z \gg z_{lim}$

This case is much more simple than the previous one. Here the kinetic equation can be written as

$$\Phi = \zeta(z) + A\nu_{lim} \int_0^{z-z_{lim}} \exp(p(\zeta(x) - \Phi)) dx$$

or

$$G = A\nu_{lim} \int_0^{z-z_{lim}} \exp(-pG(x)) dx$$

for

$$G = A\nu_{lim} \int_0^{z-z_{lim}} \exp(p(\zeta(x) - \Phi)) dx$$

It can be solved very easy. Namely, after the differentiation we come to

$$\frac{dG}{dx} = A\nu_{lim} \exp(-pG(z))$$

which can be easily integrated

$$\frac{1}{p}(\exp(pG(z)) - 1) = A\nu_{lim}z$$

The spectrum has the form

$$f \sim A \exp(-pG(z))$$

One can see that here the number of total droplets

$$N(\infty) = \int_0^\infty f(x) dx$$

is infinite. It is certainly a wrong result. The reason is inapplicability of approximation (2). The head of the spectrum is described quite satisfactory, but the tail isn't described well. Really at $n = n_\infty$ the nucleation according this approximation doesn't stop. To describe the tail we have to use the precise equation for the stationary nucleation rate

$$I_s = Z \exp(-F_c)$$

where Z is the Zeldovitch factor [6], F_c is the free energy of the critical embryo, taken in some approach but without approximate decomposition (2). For example, in capillary approximation

$$F_c = \frac{1}{3} a \nu_c^{2/3}, \quad \nu_c^{1/3} = \frac{2a}{3 \ln(\zeta + 1)}$$

where a is renormalized surface tension. Then

$$\int_0^t \nu_{lim} I_s(\zeta(t')) dt' = \Phi - \zeta(t)$$

or

$$\nu_{lim} I_s(\zeta(t)) = -\frac{d\zeta(t)}{dt}$$

The last equation can be easily integrated

$$\int_\Phi^\zeta \frac{d\zeta}{\nu_{lim} I_s(\zeta(t))} = t$$

or

$$\int_\Phi^\zeta \frac{\exp(\frac{4a^3}{27 \ln^2(\zeta+1)}) d\zeta}{\nu_{lim} Z(\zeta)} = t$$

One can get an analytical solution for the tail of spectrum having noticed that at small ζ one can decompose $\ln(\zeta + 1) \approx \zeta$. The values of ζ can not be too small, at least $\nu_c(\zeta) < \nu_{lim}$ and the behavior of Z isn't singular. So we can reduce the last equation to

$$B_2 \int \exp(B_3 \zeta^{-2}) d\zeta = t + B_1$$

with known constants $B_i, i = 1, 2, 3$. The integral can be reduced to the error function. This solves the problem of explicit solution in terms of standard special functions.

Here one has no need to observe the property (B) because this property begin to be violated only when $\nu_{lim}^{1/3}$ strongly exceeds Δz_1 and then practically all droplets attain the final values. As for the quasistationarity (property (A)) we see that $|d\zeta/dt|$ decreases in time and if (A) is observed in the initial moment of time it will be observed also later. The absence of the property (C) was taken into account just above. Instead of (D) one can state that this stage will be the last stage of the whole nucleation process in the system.

2.3 The case $\Delta_1 z \approx z_{lim}$

The intermediate case is the most complex one and has to be investigated on the base of the already presented solutions. Let the kinetic equation be rescaled to have

$$G = \Theta(z - z_{lim}) \left\{ 4 \int_{z - z_{lim}}^z (z - x)^3 \exp(-G(x)) dx + 4\nu_{lim} \int_0^{z - z_{lim}} \exp(-G(x)) dx \right\} + \Theta(z_{lim} - z) 4 \int_0^z (z - x)^3 \exp(-G(x)) dx$$

Certainly, here z_{lim} will be also rescaled.

Now we shall give the approximate method to solve this equation. The value G can be presented as

$$G = g_+ + g_-$$

where g_+ is the rescaled number of molecules in the droplets which have already attained z_{lim} , g_- is the rescaled number of molecules in all other droplets.

For further constructions we have to write approximations for g_- and g_+ . We shall start with g_-

The function g_- can be easily found on the base of iteration procedure presented for the case $\delta_1 z \ll z_{lim}$. Then

$$g_- = \Theta(z - \Delta_1 z) 4A \int_0^\infty (z - x)^3 \exp(-g_- - g_+) dx + \Theta(\Delta_1 z - z) 4A \int_0^z (z - x)^3 \exp(-g_- - g_+) dx$$

Here A is the amplitude which can differ from 1 due to the possible big value of g_+ . At the current moment this remark isn't too clear, but in any case we can say that for further purposes it is convenient to conserve A here.

Now we shall explain the last relation.

At $z < z_{lim}$ we have $g_+ = 0$ and

$$g_-(z) = 4A \int_0^z (z - x)^3 \exp(-g_-(x)) dx$$

It is important that the last equation is the closed one and it is identical to the case of unlimited growth. So, it can be successfully solved by iterations. Particularly, $g_{-(0)} = 0$, $g_{-(1)} = Az^4$, etc.

At $z \geq z_{lim}$ we have

$$g_- = 4A \int_{z - z_{lim}}^z (z - x)^3 \exp(-g_-(x) - g_+(x)) dx$$

Now we give the qualitative picture of phenomena. At the first moments of time the spectrum in the region $\rho < \rho_{lim}$ is being formed and $g_+ = 0$ but g_- is growing rather rapidly $\sim z^4$. Later the substance is going to be accumulated in droplets with $\rho = \rho_{lim}$. The growth of g_+ occurs.

If the size of cut-off z_{lim} is essentially smaller than $\Delta_1 z \equiv A^{-1/4}$ then g_- accumulates not so many molecules of substance $g_- = g_{-(in)} \equiv Az_{lim}^4 \ll 1$ and later due to the decrease of nucleation rate the value of g_- will also decrease, i.e. $g_- < g_{-(in)}$. In this case g_+ grows as

$$G_+ \approx z_{lim} 4A \int_0^{z-z_{lim}} \exp(-g_+(x) - g_-(x)) dx$$

It will grow slower than

$$g_{+(in)} = z_{lim} 4A(z - z_{lim})$$

This allows to state that

$$\frac{dg_+}{dz} < 4Az_{lim}^3$$

Then the variation δg_+ in g_+ during "the time" of establishing of the quasistationary state in the region $[0, z_{lim}]$ can be estimated as

$$\delta g_+ < \frac{dg_+}{dz} z_{lim} = 4Az_{lim}^4 \ll 1$$

In the expression for g_- for $z > z_{lim}$ the last inequality allows to take $\exp(-g_+)$ away from the integral.

Then approximately

$$g_-(z) = 4A \exp(-g_+(z)) \int_{z-z_{lim}}^z (z-x)^3 \exp(-g_-) dx$$

and on the base of initial iteration approximation

$$g_-(z) = A \exp(-g_+(z)) z_{lim}^4$$

Now we shall get expression for g_+ . We shall get for g_+ the following approximate equation

$$g_+ = 4Az_{lim}^3 \int_0^{z-z_{lim}} \exp(-g_-(x) - g_+(x)) dx$$

Here z is the current "moment of time", z_{lim} is the "moment" when the spectrum attains z_{lim} .

Here we are interested in the other characteristic scales of time which are greater than $1/(4Az_{lim})$. At these times we can suppose that $\exp(-g_-)$ is approximately constant and take it out of the integral. Then approximately

$$g_+ = 4Az_{lim}^3 \exp(-g_-) \int_0^{z-z_{lim}} \exp(-g_+(x)) dx$$

When g_- is essential (i.e. $\exp(-g_-)$ is small) then g_+ isn't necessary and we can take out $\exp(-g_-)$. But when g_- is small, then $\exp(-g_-) = 1$ and we can also take it out. The substance consumption in g_- occurs in the avalanche manner.

We can get solution of this equation quite analogously to the case $\Delta_1 z \gg z_{lim}$ but here the initial conditions will be another

$$g_-|_{x=z-z_{lim}} = 0$$

Solution will be

$$\frac{dg_+}{dz} = 4Az_{lim}^3 \exp(-g_-) \exp(-g_+)$$

and

$$\exp(g_+) - 1 = 4Az_{lim}^3 \exp(-g_-)(z - z_{lim})$$

The spectrum will be

$$f = 4A \exp(-g_-) / \exp(g_+)$$

or

$$f = 4A \exp(-g_-) / (1 + 4Az_{lim}^3 \exp(-g_-)(z - z_{lim}))$$

In the initial approximation we consider $A = 1$ and get

$$f = f_0 \equiv 4 \exp(-z_{lim}^4) / (1 + 4z_{lim}^3 \exp(-g_-)(z - z_{lim}))$$

Then we take $g_- = z_{lim}^4$ and get

$$f = f_0 \equiv 4 \exp(-z_{lim}^4) / (1 + 4z_{lim}^3 \exp(-z_{lim}^4)(z - z_{lim}))$$

It is necessary refine expression for the spectrum obtained in the zero approximation. We have to take into account that g_+ is formed under the influence of g_- . But the spectrum in the last expression is written through g_- (but not through g_+). Here is the difficulty. We shall come it over via the special approximate approach. At first we assume that g_- (but not the g_+) is formed with the renormalized intensity. We take $\exp(-\alpha z_{lim}^4)$ instead of $\exp(-z_{lim}^4)$. It is evident that we do this only in the first factor which is responsible for the influence of g_- . So, we get

$$f = 4 \exp(-\alpha z_{lim}^4) / (1 + 4z_{lim}^3 \exp(-z_{lim}^4)(z - z_{lim}))$$

For α we have to take the renormalized amplitude. The natural candidate for this amplitude is f_0 . As the result we come to the following expression for spectrum

$$f_1 = F(f_0) \equiv f_0 K$$

where

$$K = \frac{\exp(-f_0 z_{lim}^4)}{\exp(-z_{lim}^4)} \\ f_0 \frac{\exp(-z_{lim}^4)}{1 + 4z_{lim}^3 \exp(-z_{lim}^4)(z - z_{lim})}$$

Now let us realize what have we done. In reality we had to take into account the inverse influence, i.e. to take into account that g_+ is formed under the

influence of g_- , but not the influence of g_+ on g_- . To take into account the inverse influence we shall use the inverse transformation F^{-1} . So, approximately

$$f = F^{-1}(f_0)$$

We can calculate this transformation rather easy

$$f = F^{-1}(f_0) = \frac{f_0}{K}$$

This will solve the problem of the adequate construction of the approximate spectrum.

The error of this approximation in the total droplets number is drawn in Figure 2. Certainly, we can not calculate here the total number of droplets (it will be infinite and has to be corrected by the way described in the previous subsection). As the final value z_{fin} the magnitude 10 has been chosen. The last belongs to the asymptotic period. One can see that the relative error in the droplets number is small.

Statements (A), (B), (C) take place here. Statement (D) isn't necessary.

2.4 Further nucleation

The case $\Delta_1 z \ll z_{lim}$ requires the analysis of the further nucleation. This analysis isn't too complex. On the base of ζ_{fin-1} we can calculate the length $\Delta_2 z$ as

$$\Delta_2 z = \Delta_1 z(\zeta_{fin-1})$$

i.e. we use the same formula but with ζ_{fin-1} instead of Φ . In expression (4) there is an amplitude of spectrum A which is a very sharp function of supersaturation. So, we see that

$$\Delta_1 z \ll \Delta_2 z$$

This strong inequality allows to neglect the time interval $[0, \Delta_1 z \tau / \Phi]$ in the nucleation at ζ_2 . Then the situation is reduced to the nucleation with initial supersaturation ζ_2 . We have to repeat the steps of the three previous sections. Again we can come to the possibilities (B) and (C). The possibility (A) cannot take place because the inequality

$$\exp(N_1 x_{lim}^3 / 4) \ll x_{lim}$$

doesn't take place. Here the l.h.s. is $\Delta_2 z$ in rescaled units, N_1 has to be put to 0.9, the coefficient 4 in denominator came from the power 1/4 in (4), the parameter x_{lim} has to satisfy $x_{lim} > 2 \div 3$.

So, we see that the structure of spectrum isn't too complex - the plateau, the region of partial collapse of surplus substance and may be the tail.

The analysis of nucleation after instantaneous creation of a metastable state has been completed.

3 Nucleation under the smooth behavior of external conditions

The straightforward generalization of kinetic equation to the case of smooth change of external conditions leads to the following kinetic equation

$$\Phi(z) = \zeta(z) + \quad (7)$$

$$A \int_{z-z_{lim}}^z (z-x)^3 \exp(p(\zeta(x) - \Phi_*)) dx + A\nu_{lim} \int_{-\infty}^{z-z_{lim}} \exp(p(\zeta(x) - \Phi_*)) dx$$

Here $\Phi(z)$ is ideal supersaturation, i.e. the supersaturation which should take place in the system without any processes of vapor consumption and heat release effects. The value of Φ at some characteristic moment t_* will be marked as Φ_* . We shall choose t_* later. The number of droplets (in renormalized units) will be calculated as

$$N(z) = \int_{-\infty}^z \exp(p(\zeta(x) - \Phi)) dx$$

Under the unlimited growth of droplets the period of nucleation is well localized in time. Moreover it is rather short in time which allows to linearize the ideal supersaturation during this period. Here the process of nucleation cannot be localized in time, it is seen simply by the fact that the number of droplets in a liquid phase is limited from above by $N\nu_{lim}$. Then to compensate the "action" of external conditions it is necessary to have nucleation again and again.

To present concrete calculations we suppose that the ideal supersaturation can be linearized

$$\Phi(z) = \Phi_* + \frac{d\Phi(z)}{dz} \Big|_{z=0} z$$

but now is is no more than a model. Later we shall see how to construct the theory for rather arbitrary behavior $\Phi(z)$.

But even with this linearization the situation here can not be solved by a simple generalization of the ordinary iteration procedure because here process isn't limited in time.

3.1 Rescaling

Kinetic equation (7) can be written in the following form

$$g = \int_{-\infty}^{z-x_{lim}} x_{lim}^3 f(x) dx + \int_{z-x_{lim}}^z (z-x)^3 f(x) dx$$

with $x_{lim} = z_{lim}$ and a spectrum $f(x)$

$$f(x) = a \exp(bx - g(x))$$

It is essential that after the evident rescaling one can put $a = 1$ and $b = 1$. The third parameter x_{lim} remains and this leads to the absence of universality.

Restriction $a = 1$, $b = 1$ doesn't lead to the special meaning of the point $z = 0$ (in homogeneous condensation $z = 0$ was the point of the maximum of supersaturation, in heterogeneous condensation $z = 0$ was the point where the half of droplets have been appeared). One has simply require that $\Phi(z = 0)$ isn't too far from the maximum of supersaturation. This fact can be also analytically proved here.

When $x_{lim} = \infty$ as one can get the half-width of spectrum by condition

$$\Delta z = 1$$

3.2 Pulse regime

When $x_{lim} \gg 1$ the process of nucleation can be described rather simple. To describe the first peak of the nucleation intensity we have to solve equation without limit of growth. This case is well known and can be solved both by iterations [8] and by universal solution [4]. Thus, we get N_1 - the number of droplets formed in the first peak. One can see $N_1 \sim 1$. Then the supersaturation ζ continues to fall until $z \sim x_{lim}$. The inequality $x_{lim} \gg 1$ allows here to speak about the well formed peak of nucleation intensity and to use the standard procedure of unlimited growth. At $z \sim x_{lim}$ the supesaturation begins to grow. At $z \sim x_{lim}$ we have $f \sim \exp(x_{lim} - N_1 x_{lim}^3) \ll 1$. At $z \sim N_1 x_{lim}^3$ the second peak of nucleation begins.

The second peak of nucleation can be described absolutely analogously to the first one. So, we have the set of identical peaks. The nucleation occurs in the pulse regime.

This regime is shown in Figure 3.

3.3 Smooth regime

The opposite situation when $z_{lim} \ll 1$ can be also solved analytically. Here kinetic equation can be written as

$$\Phi(z) = \zeta(z) + A\nu_{lim} \int_{-\infty}^{z-z_{lim}} \exp(p(\zeta(x) - \Phi_*)) dx \quad (8)$$

and

$$\Phi(z) = \zeta(z) + A\nu_{lim} \int_{-\infty}^z \exp(p(\zeta(x) - \Phi_*)) dx \quad (9)$$

After differentiation with account of linearization we have

$$\frac{dg}{dz} = A\nu_{lim} \exp(bz - pg(z))$$

In our units $p = 1$, $A\nu_{lim} = 1$, $b = 1$. Integration with initial conditions

$$g(z = -\infty) = 0$$

gives

$$\exp(g(z)) = A\nu_{lim} \exp(z) + 1$$

This value will be marked as g_{st} . Then the spectrum f will be

$$f = f_{st} \equiv \exp(x - \ln(\exp(x) + 1)) \quad (10)$$

At $x \rightarrow \infty$ we see $f_{st} \rightarrow f_{st \text{ lim}} \equiv 1$.

This spectrum f_{st} and the example of numerical solution are drawn in Figure 4.

These limit situations will form the base for description of nucleation in all situations. But here we have to stress two features:

- The limit solutions have to be radically modified. The force of the already presented methods for these solutions isn't sufficient to give the total description.
- Description of the base of the iteration method can not be suitable because the process isn't restricted in time.

At first we shall present the general structure of methods and then we shall show how to determine the elements included in these approaches.

3.4 Advanced pulse regime

To describe situations with $x_{lim} \geq 2$ and $|x_{lim} - 2| \ll 2$ one has to use the rescaled peaks approach. This approach is based on the following simple considerations.

Due to the previous analysis we shall approximate the spectrum by several peaks. Every peak is formed by some external effective source (initiated both by external conditions and by the action of the tail of the previous peak). The distance between peaks of nucleation is approximately

$$\Delta_f x = Nx_{lim}^3$$

where N is the number of droplets formed in the previous peak. Certainly, between different peaks the distance can be different because N will be different, but the suitable approximation is to consider N to be the ideal value, i.e. at the first peak. The last formula will be rather evident if we notice that the action of external conditions has simply to compensate the loss of substance which is equal to Nx_{lim}^3 .

Here we shall present a recurrent procedure to calculate peaks of nucleation. Suppose that we have described the current peak and know the coordinate of maximum x_m .

Now we have to rescale the amplitude of the next peak. We neglect the non-linear behavior of effective source. Then the next peak will be similar after rescaling to the previous one. But without rescaling in the same units the next peak will have a new (ordinary smaller) height and another width (ordinary wider). So, now we have to determine the new intensity b' of the effective source (the initial intensity was $b_0 = 1$).

We know the expression for intensity of vapor consumption by droplets i.e. dg/dz :

$$\frac{dg}{dz} = 3A \int_{z-x_{lim}}^z (z-x)^2 \exp(x-g(x)) dx$$

The subintegral function has the form

$$(z-x)^2 \exp(x-g(x))$$

and approximately has maximum at $(z-x) = \rho_a = 2$ for $x_{lim} > 2$ and $(z-x) = \rho_a = x_{lim}$ for $x_{lim} < 2$ (here we can put $z = 0$ at maximum because this choice will result only in parameters but not in the spectrum form).

The current peak have coordinate x_m , the next peak will have coordinate $x_m + \Delta_f x$. The maximum of subintegral expression for $d\rho/dz$ for the next peak will be attained at $x_b = x_m + \Delta_f x - x_a$. The main effect is connected with a property that at $x = x_b$ the essential quantity of droplets from the previous peak has attained the value x_{lim} . But not all droplets have attained this value. So, the supersaturation ζ lies higher than the supposed value

$$b_0 z - N x_{lim}^3$$

which would ensure the similarity of the next peak to the previous one.

The supersaturation at the corresponding coordinate $x_c = x_m - x_a$ for the previous peak was lower than at the current peak.

We suppose that at $x = x_b + x_a = x_m + \Delta_f x$ approximately corresponding to the coordinate of the next peak all droplets of the previous peak will attain the limit value $N x_{lim}^3$ and there will be no difference between the value of effective ideal supersaturation (the supersaturation imaginary formed without droplets of the last peak taken into account) Ω at x_m and at $x_m + \Delta_f x$

$$\Omega(x_m) = \Omega(x_m + \Delta_f x)$$

The effective intensity b' of the external source can be approximated as

$$b' \sim \frac{\Omega(x_m + \Delta_f x) - \Omega(x_m + \Delta_f x - x_a)}{x_a}$$

and have to be compared with

$$b_0 \sim \frac{\Omega(x_m) - \Omega(x_m - x_a)}{x_a}$$

Then taking into account

$$|\Omega(x_m + \Delta_f x - x_m) - \Omega(x_m + \Delta_f x)| \ll 1$$

and

$$|\Omega(x_m) - \Omega(x_m - \Omega(x_m - x_a))| \sim x_a \geq 1$$

one can come to

$$b' = b_0 - \frac{\Delta\zeta}{x_a}$$

where

$$\Delta\zeta = \Omega(x_m + \Delta_f x - x_a) - \Omega(x_m - x_a)$$

Since $b_0 = 1$ one can come to

$$b' = 1 - \frac{\Delta\zeta}{x_a}$$

We can express $\Delta\zeta$ as

$$\Delta\zeta = \ln \tilde{f}(x_b) - \ln \tilde{f}(x_c) = \ln \frac{\tilde{f}(x_b)}{\tilde{f}(x_c)}$$

where \tilde{f} is the spectrum corresponding to the external ideal supersaturation. Since $x_a > 1$ one can see that the effect of the influence of the current peak is negligible and

$$\tilde{f}(x_b) = f(x_b)$$

$$\tilde{f}(x_c) = f(x_c)$$

So, finally we have the following formula for b' :

$$b' = b_0(1 - \frac{\zeta_a}{x_a})b$$

where ζ_a is the difference of supersaturations at $x = x_c \equiv x_m - x_a$ and at $x = x_b \equiv x_m - x_a + \Delta_f x$ calculated for the previous peak. Here x_m is the coordinate of the maximum of the supersaturation. The difference $x_b - x_c$ can be calculated as

$$x_b - x_c = \ln\left(\frac{f(x_b)}{f(x_c)}\right)$$

This completes the procedure. The first peak calculations have to be performed in explicit manner.

The calculations are presented in Figure 5. We see that the calculated peaks are very close to the real solution.

Even such simple rescaling brings a rather accurate result. When $x_{lim} > 2$ the accuracy will be better. It can be proved analytically. The simple account of variations of $\Delta_f x$ will give the better accuracy also. All other errors can be taken into account by the standard perturbation technique.

3.5 Advanced smooth regime

We see that already at $x_{lim} = 2$ the first peak lies not so far from the stationary solution (10). Later all peaks will be even smaller than the first one. So, we can consider $(f - f_{st})/f_{st}$ as the small parameter and linearize the kinetic equation over this parameter. Then this solution can be solved analytically and will give

the oscillations relaxing to f_{st} . We can avoid these long analytical derivations and simply draw the relaxation oscillations

$$f_{osc} = f_{st} + k_1 \exp((x - x_m)/k_2) \cos((x - x_m)/\Delta_f x)$$

with two parameters k_1 and k_2 . The arguments for derivation of $\Delta_f x$ takes place here also.

Parameters k_1 and k_2 can be determined by a coincidence of approximate and real solution at maxima of two first peaks. We choose maxima for coincidence of real solution and approximate solution because namely here the intensity of nucleation has maxima. The first local minima demonstrates the deviation of approximate solution from the real one but here the intensity of nucleation is small.

This solution is drawn in Figure 6. One can see that precise solution is very close to approximate one.

3.6 Iterations to determine parameters

Now we know the methods to describe nucleation adequately, but parameters in these approximations are unknown and our next task will be to determine these parameters. To do this we have to know the evolution during several first peaks of nucleation. In the advanced pulse method we have to know the evolution during the first peak including the back side of the peak and in the advanced relaxation method we have to know the positions and values of two first maximums. These characteristics will be determined on the base of iteration methods. But here the iteration methods can not be got by direct generalization of already presented procedures in the case of condensation under the pure free molecular regime of vapor consumption [8], [4]. Really, even in the pure free molecular regime it is difficult to describe even the back side of spectrum on the base of standard iterations and here we need to describe the second peak. The limitation of growth will also diminish the converging power of iterations. So we need to reexamine the iteration procedure.

The evolution equation can be rewritten as

$$g = \Theta(z - z_{lim}) \left\{ \int_{z - z_{lim}}^z (z - x)^3 \exp(x - g(x)) dx + \nu_{lim} \int_0^{z - z_{lim}} \exp(x - g(x)) dx \right\} + \Theta(z_{lim} - z) \int_0^z (z - x)^3 \exp(x - g(x)) dx$$

The initial standard iteration procedure can be determined as

$$g_{i+1} = \Theta(z - z_{lim}) \left(\int_{z - z_{lim}}^z (z - x)^3 \exp(x - g_i(x)) dx + \nu_{lim} \int_0^{z - z_{lim}} \exp(x - g_i(x)) dx \right) + \Theta(z_{lim} - z) \int_0^z (z - x)^3 \exp(x - g_i(x)) dx$$

It will converge at every initial approximation.
 As suitable initial approximations one can propose

$$g_0 = 0$$

or

$$g_0 = g_{st}$$

$$g_{st} = 0 \text{ at } x < \ln(f_{st \text{ lim}}), \quad g_{st} = x \text{ at } x \geq \ln(f_{st \text{ lim}}).$$

Since here it will be impossible to take only two first iterations there is no special significance what approximation we shall use. We prefer to use the first one because here the chain of inequalities

$$g_0 < g_2 < \dots < g_{2i} < \dots < g < \dots < g_{2i+1} < \dots < g_3 < g_1 \quad (11)$$

for every fixed x is observed. These iterations are shown in Figure 7.

Decomposition in iterations

The analytical calculation of iterations will stop at the second step. For the unlimited free molecular regime this number of iteration is sufficient, but here we have to calculate the next iterations. It is possible analytically if we choose the decomposition of exponent in the subintegral function. But here the following difficulty appear. The value of g goes to infinity and it isn't possible to decompose $\exp(-g(x))$ over $g(x)$. The other possibility is to decompose $\exp(x - g(x))$ over $x - g$ near some characteristic value of the exponent argument. But at $x \rightarrow -\infty$ the value of g goes to zero and the spectrum looks like $\exp(-|x|)$. Then it is impossible to use the second decomposition at initial moments of time (i.e. at negative x). But this very period drives the evolution during the first peak of nucleation and, thus, plays the main role in nucleation description. So, the pure second approach can not lead to a suitable result. So, we need to give here more sophisticated approach.

We shall act in the following manner. Already the first iteration gives us the approximate position of the first maximum $x_{max \ 1}$ and the value of this maximum $f_{max \ 1}$. Then we propose the following procedure

- When $x < x_{max \ 1}$ then

$$\exp(-g) \approx \sum_{i=0}^4 \frac{(-g)^i}{i!}$$

Here the first four terms are taken into account. It is sufficient to ensure the high relative accuracy.

- When $x \geq x_{max \ 1}$ then

$$\exp(x - g) \approx \exp(\zeta_{base}) \sum_{i=0}^4 \frac{(x - g - \zeta_{base})^i}{i!}$$

where

$$\zeta_{base} = \ln\left(\frac{f_{max\ 1} + f_{st\ lim}}{2}\right)$$

is the base of decompositions.

Here decomposition of the corresponding exponent is limited also by the first four terms.

Then the iterations can be calculated analytically at every step and they give the adequate approximation for the solution. They converge to the solution of kinetic equation where instead of \exp one should write the presented approximation. Already the four first terms of decomposition of the corresponding exponent ensure the high accuracy.

These iterations are shown in Figure 8.

We see that already the several first iterations give the practically precise positions of the first maximum and the first minimum $f_{min\ 1}$ at $x_{min\ 1}$. Later we see that iterations converge but every new iteration gives the "step" of coincidence with the real solution which becomes smaller and smaller. The reason of this failure is the following: really, the precise solution doesn't go far from $f_{st\ lim}$ and decomposition works, but every iteration inevitably goes to zero or to infinity and on every iteration the decomposition doesn't work. This error leads to crisis in convergence of iterations. So, we need to modify iterations.

Cut-off of iterations

Now we know $f_{max\ 1}$ and $f_{min\ 1}$ and can use these characteristics. One can analytically prove that for every $x > x_{max\ 1}$

$$f_{min\ 1} < f < f_{max\ 1}$$

Then we can require that before we use decomposition the following cut-off

- When $\exp(x - g_i(x)) > f_{max\ 1}$ we should take instead of $\exp(x - g_i(x))$ the value the constant $f_{max\ 1}$ and fulfill no further decompositions⁴.
- When $\exp(x - g_i(x)) < f_{min\ 1}$ we should take instead of $\exp(x - g_i(x))$ the value the constant $f_{min\ 1}$ and fulfill no further decompositions.
- When $f_{min\ 1} < \exp(x - g_i(x)) < f_{max\ 1}$ no special actions are required and we have to make the mentioned decompositions.

The convergence of new iterations is higher than the convergence of previous iterations. New iterations evidently converge to the real solution⁵. Also it is very easy to estimate rigorously the error of decomposition because now we have an estimate $f_{min\ 1} \leq f_i \leq f_{max\ 1}$ for every x and for every i .

To complete the description of iterations one can prove the following important statements

⁴One can see that iterations escape from the real solution.

⁵with corresponding decomposition.

- The cut-off iterations without decompositions converge to the real solution of kinetic equation and they converge faster than the first-type iterations. The chains of inequalities (11) remain valid for the cut-off iterations without decompositions.
- The iterations with decompositions converge to the solution of kinetic equation where function \exp is treated according to the mentioned decompositions. The chains of inequalities (11) remain valid (here g is solution of kinetic equation where the function \exp is treated according to the mentioned decompositions)⁶.

For practical needs one can show that for $x_{lim} \leq 2$ already the sixth iteration ensures the correct values of $f_{max\ 1}, x_{max\ 2}$ and $f_{max\ 2}, x_{max\ 2}$ (the value and the coordinate of the second peak)⁷. This is all we need to construct the relaxation oscillations.

Behavior of the cut-off iterations is shown in Figure 9. One can see the high rate of convergence.

When $x_{lim} > 2$ we can use the advanced pulse method and here we need to describe only the first peak. It can be done by the first four iterations (Really, if it would be necessary to get the coordinate of the second peak we might have difficulties because of the very small value of $f_{min\ 1}$).

This solves the problem to get the parameters of approximation and completes the description of the nucleation under the break of the blow-up growth.

⁶To show this we have to see that decomposition of \exp conserves the monotonious properties. It can be shown if we differentiate the approximation and note that the derivative of approximation is the approximation for the derivative of exponent. Then with the necessary terms taken into account and with account that $f_{min\ 1} \leq f_i \leq f_{max\ 1}$ this derivative can be made positive. Then the monotonious properties remain even after decompositions.

⁷When $x_{lim} < 2$ then the iterations will approximate these values even better then at $x_{lim} = 2$. It can be proved analytically.

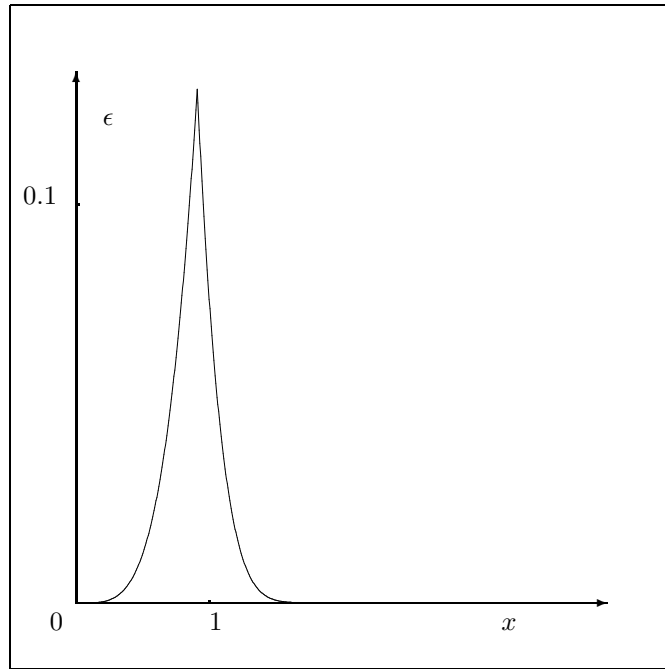


Figure 1
Relative error ϵ of initial approximation

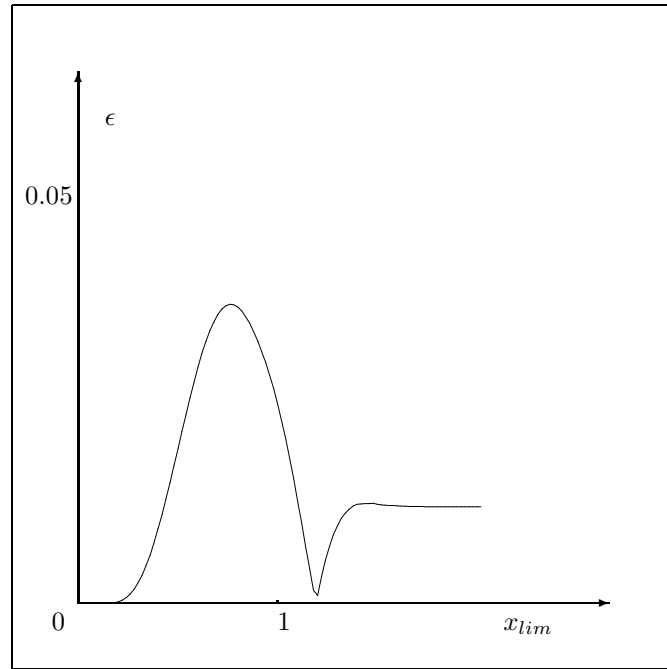


Figure 2
Relative error ϵ of the special approximation

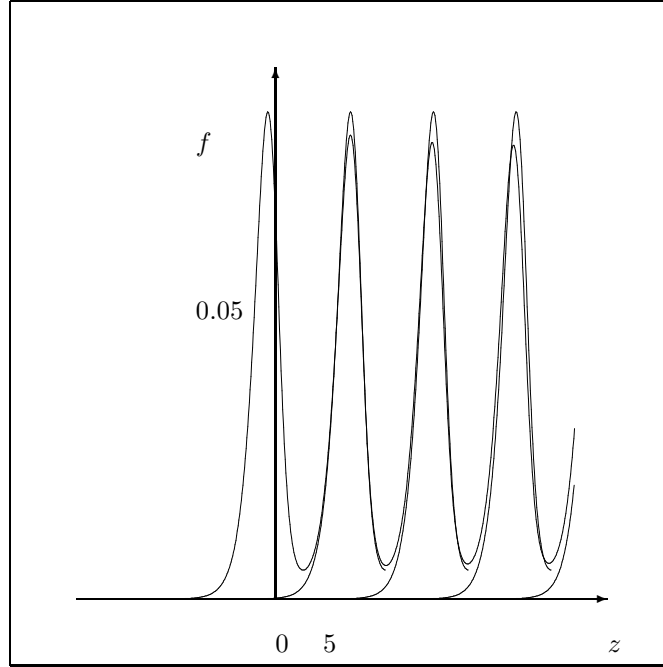


Figure 3

Peaks of spectrum in impulse regime $x_{lim} = 2.6$ (if it will be greater we can not see the difference between the precise and the approximate solution). The variable z is going until 30. Approximate peaks lie higher than the precise solution, The last peak lies at greater z than the precise solution.

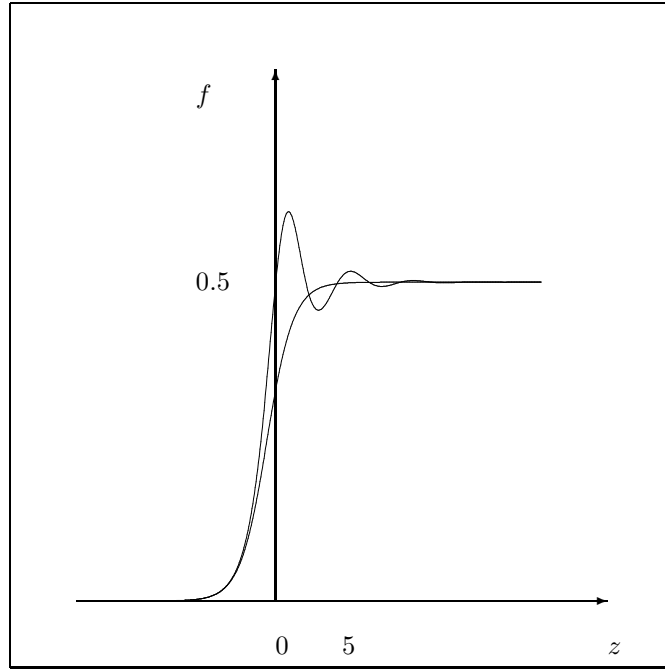


Figure 4

Peaks of spectrum in smooth regime $x_{lim} = 1.25$ (if it will be smaller we can not see the difference between precise and approximate solution). The value z is going until 20. The precise solution oscillates, the approximate solution is flat.

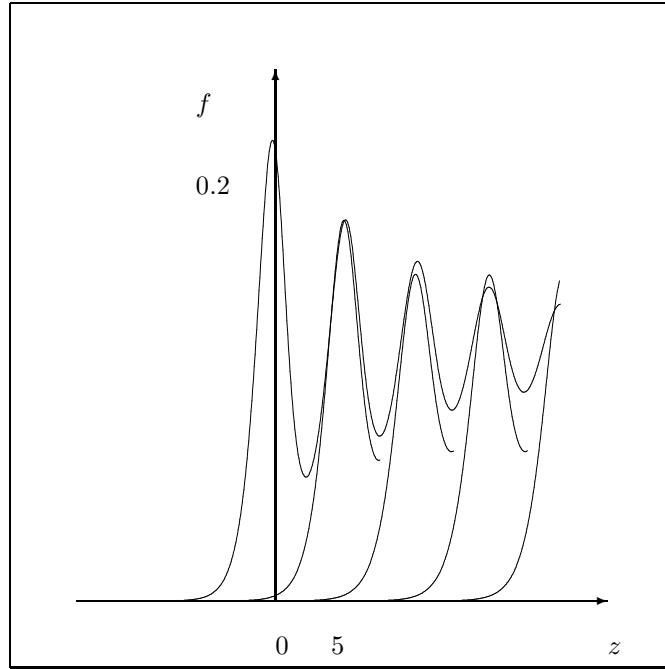


Figure 5

Peaks of spectrum and advanced peaks at $x_{lim} = 2.0$.

The value z is going until 25. Approximate peaks are separate lines. The global continuous line is the precise solution.

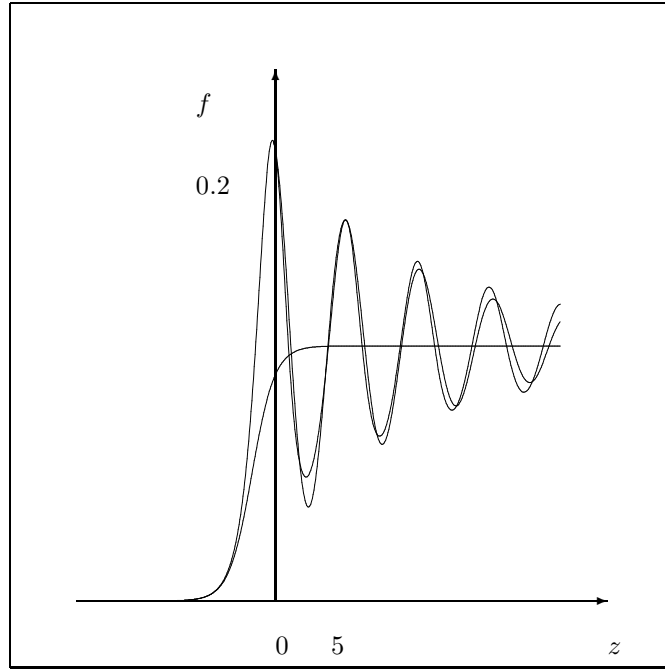


Figure 6

Spectrum and the relaxaiton solution at $x_{lim} = 2$.

The value z is going until 25. Approximate solution has more symmetric peaks than the precise one. Only in the first negative gap one can see the difference between approximate and precise solutions.

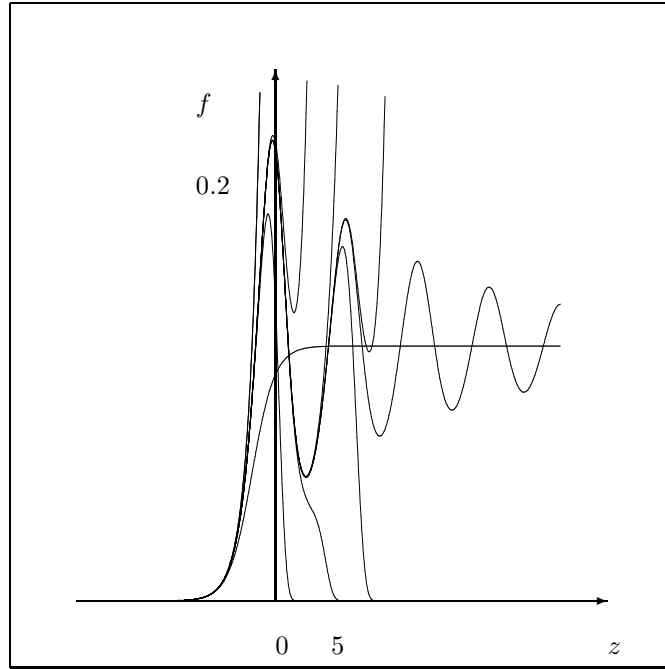


Figure 7

Precise solutions and iterations (calculated numerically) without decompositions for $x_{lim} = 2$ (the worst situation). Iterations are going near precise solution and then fall very rapidly down or grow up to infinity. The higher is the iteration number the longer it is going near the real solution

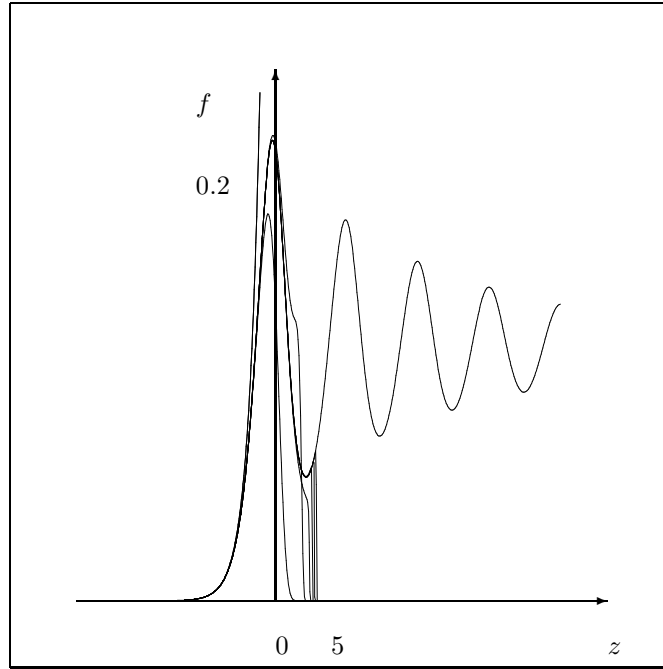


Figure 8

Precise solutions and iterations with decompositions (calculated analytically). Here $x_{lim} = 2$. (the worst situation) Iterations are going near precise solution and then very rapidly fall down or grow up to infinity. With the growth of iteration number there is practically no effect in the length of coincidence between the iteration and the precise solution.

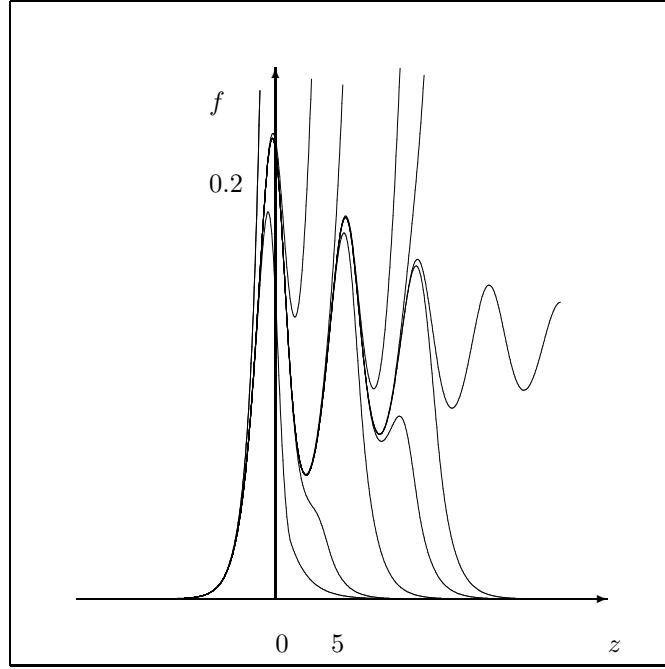


Figure 9

Precise solutions and iterations with decompositions with the cut-off. Here $x_{lim} = 2$ (the worst situation). Iterations are going near precise solution.

With the growth of iteration number the length of coincidence between the iteration and the precise solution grows also rather rapidly.

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